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## **Monte Carlo Simulations of Atom Transfer Radical (Homo)Polymerization of Divinyl Monomers: Applicability of Flory-Stockmayer Theory**

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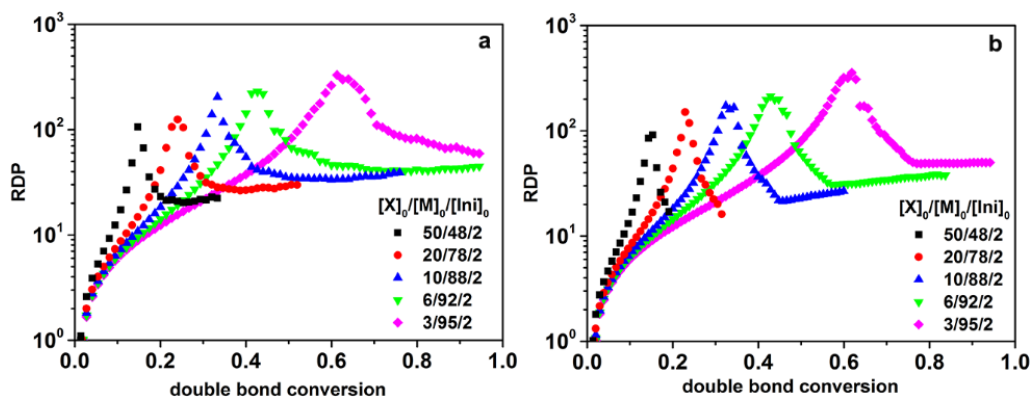


Figure S1. Simulation for ATRcP of monovinyl monomers and divinyl monomers.

The dependence of  $RDP$  plotted vs. double bond conversion, obtained from (a) **w.c.** model and (b) **wo.c.** model for various  $[X]_0/[M]_0/[Ini]_0$ .

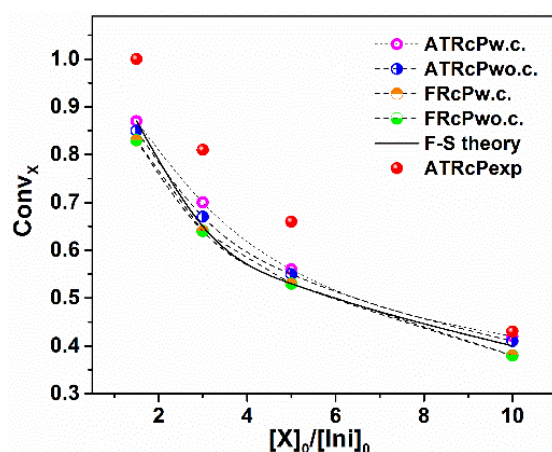


Figure S2. Comparison of the gel points ( $Conv_x$ ) for various initial molar ratios of divinyl monomer to initiator  $[X]_0/[Ini]_0$ , obtained from ATRcP, FRcP simulations and F-S theory.

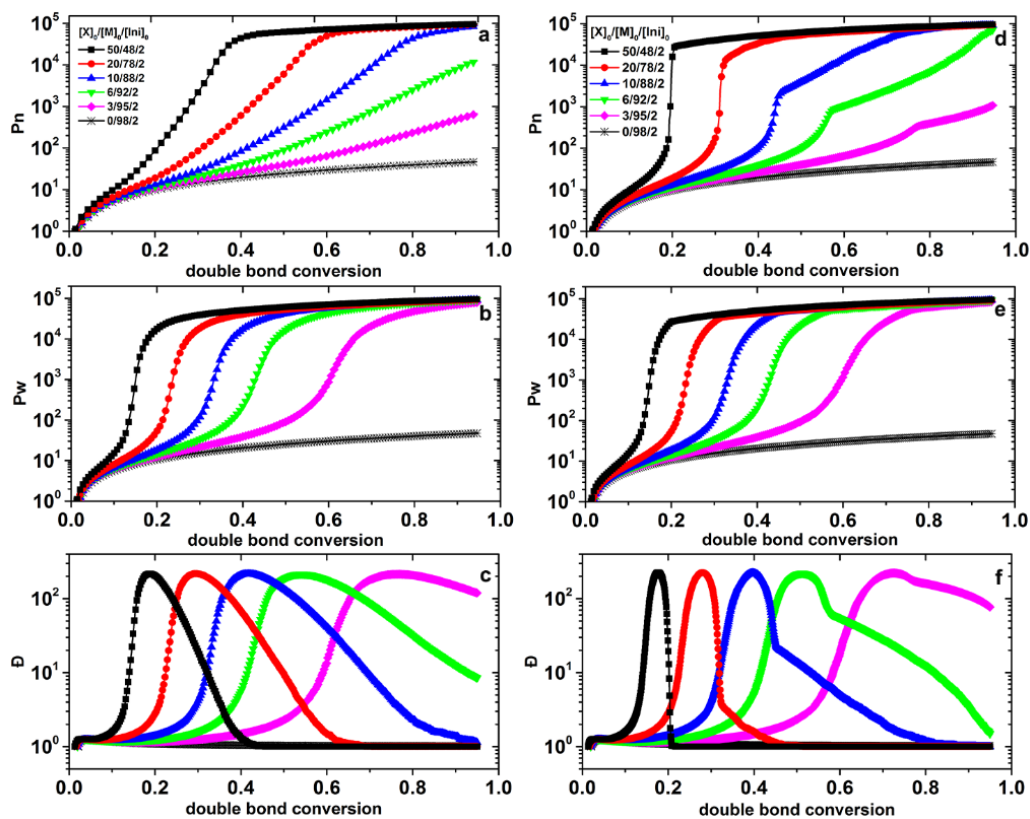


Figure S3. Simulation for ATRcP of monovinyl monomers and divinyl monomers. The growth of  $P_n$  with double bond conversion for (a) **w.c.** model and (d) **wo.c.** model. The growth of  $P_w$  with double bond conversion for (b) **w.c.** model and (e) **wo.c.** model. The growth of  $D$  with double bond conversion for (c) **w.c.** model and (f) **wo.c.** model.

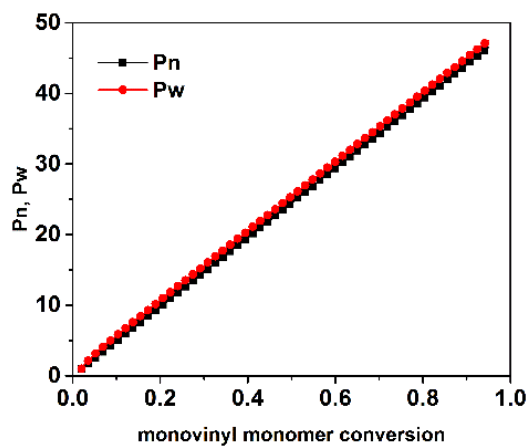


Figure S4. Simulation for ATRP of monovinyl monomers. The linear growth of  $P_n$  and  $P_w$  with monovinyl monomer conversion.

Table S1. Comparison of gel points of ATRcP of monovinyl and divinyl monomers obtained from experiments, F-S theory and different simulation models.

$[X]_0/[M]_0/[Ini]_0$	<b>w.c.</b> sim <sup>a</sup>		<b>wo.c.</b> sim <sup>a</sup>		ATRP exp <sup>b</sup>	F-S calc <sup>b</sup>		DLL w.c. <sup>b</sup>		DLL wo.c. <sup>b</sup>	
	Conv <sub>d</sub>	Conv <sub>x</sub>	Conv <sub>d</sub>	Conv <sub>x</sub>		Conv <sub>d</sub>	Conv <sub>x</sub>	Conv <sub>d</sub>	Conv <sub>x</sub>	Conv <sub>d</sub>	Conv <sub>x</sub>
20/78/2	0.24	0.42	0.23	0.41	0.43	0.22	0.40	0.38	0.57	0.34	0.55
10/88/2	0.33	0.56	0.32	0.55	0.66	0.32	0.53	0.50	0.71	0.46	0.68
6/92/2	0.44	0.70	0.43	0.67	0.81	0.41	0.65	0.62	0.83	0.56	0.78
3/95/2	0.64	0.87	0.62	0.85	1.0	0.58	0.82	0.83	0.95	0.76	0.90

<sup>a</sup>The values were calculated in this work. <sup>b</sup>The values for  $Conv_x$  were taken from ref.

<sup>[1,2]</sup>, and the values for  $Conv_d$  were calculated in this work.

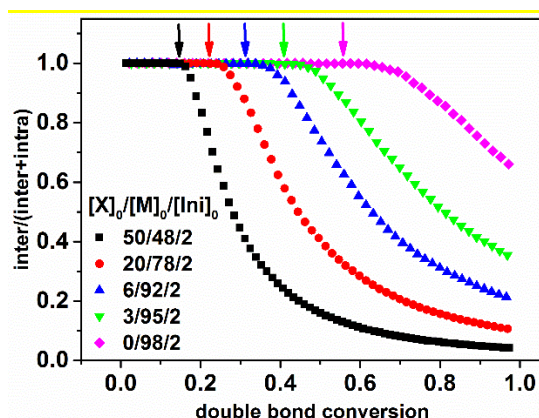


Figure S5. Simulation for ATRcP of monovinyl monomers and divinyl monomers using **w.c.** model shows the ratio of intermolecular crosslinking formed at different conversions. Ratio of intermolecular crosslinks per chain to all crosslinks per chain versus double bond conversion. Arrows indicate gel points.

**Reference:**

- (1) H. Gao, P. Polanowski, K. Matyjaszewski, *Macromolecules* **2009**, *42*, 5925-5932.
- (2) P. Polanowski, J. K. Jeszka, K. Krysiak, K. Matyjaszewski, *Polym. (United Kingdom)* **2015**, *79*, 171-178.